

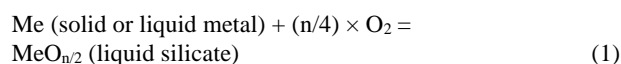
THE EFFECT OF OXYGEN FUGACITY AND PRESSURE ON SOLUBILITIES OF NICKEL AND COBALT IN SILICATE MELTS IN THE PRESENCE OF GRAPHITE AND (CO,CO₂) FLUID. A. A. Kadik (Vernadsky Institute of Geochemistry and Analytical Chemistry, RAS, Kosigin St. 19, Moscow V334, Russia, and J. R. Holloway, Departments of Chemistry and Geology, Arizona State University, Tempe, USA.

It has been known for some time that siderophile element abundance in the Earth's mantle is high for metal to have been in equilibrium with silicate particularly if equilibrium was established at low pressure and temperatures near the surface of the accreting Earth [1–6]. Although a variety of models have been proposed to explain this apparent disequilibrium, none has been entirely satisfactory. In particular, the mantle's near-chondritic ratio of Ni to Co is hard to explain. Here we report experimental results on solubilities of Ni and Co in silicate melts in the presence of graphite and (CO,CO₂) fluid at 1350–1400°C and 7–15 kbar, which show that elements become more siderophile with increasing pressure along the C-CO-CO₂ oxygen buffer.

Problem: Theories of the formation of the Earth strongly suggest that the Earth should have been substantially molten during and immediately after accretion, when molten alloy and molten silicate underwent gravitational separation [2,7]. It is expected that during large-scale melting the C-bearing mantle has become progressively oxidized, resulting perhaps largely from the preferred loss of H and C [4,8,9]. The experimental work on metal-silicate partition coefficients shows that the mantle oxidation in this case should be critical to an understanding of fractionating of highly siderophile elements [4–6]. It was demonstrated that the compositions metal particles should be drastically modified by the melting and the oxygen fugacity evolution [10]. This study was undertaken to examine the effect of pressure and elemental C and (CO,CO₂) fluid on equilibria between coexisting silicate and (Ni,Co) metallic C-bearing liquids. It is expected that the addition of free C and CO,CO₂ to the system will affect the apparent partition coefficient by diluting the liquid metal with C and possible formation of metallic C-bearing species in the melt and the CO-CO₂ vapor phase [11].

Results: Experimental conditions, electron microprobe analyses, and results are presented in Table 1. Both silicate and C-bearing metal liquids, on quenching, formed discrete relatively large masses of metal intergrowth and glass with a few clinopyroxene crystals in some runs. The 15-kbar experiment was about 90% crystalline. Graphite occurred both as stable crystals in contact with silicate and metal melts and as quench crystals in the metal phases. The Ni and Co C-bearing alloys consisted of a quench texture of two metals. One metal phase was enriched in Pt (5–10 wt%) and low in C (0.5 wt%), while the other phase was low in Pt (0.1–2 wt%) and high in C (1.5 wt%). Either In or CO made up the remainder of the metal phases. The C contents are minimum estimates because a significant amount of quench graphite exsolved from the metal.

Discussion: The transition of a neutral metal atom from metal into silicate melt is accompanied by oxidation according to the following equation



where n is the valence of the metal ion. The equilibrium constant of reaction (1) is given by

$$K = [(X(\text{MeO}_{n/2}) \times \gamma(\text{MeO}_{n/2})) / (a(\text{Me}) \times (f\text{O}_2)^{n/4})] \quad (2)$$

where X_i , a_i , and γ_i , denote mole fraction, activity, and activity coefficient ($a_i = \gamma_i \times X_i$) (liquid silicate). If equilibria of pure metals with silicate melts are considered, $a(\text{Me}) = 1$, we can obtain for the metal melt partition coefficient for Me, $D(\text{metal/silicate})$

$$\log D(\text{metal/silicate}) = \log [X(\text{Me})/X(\text{MeO}_{n/2})] = \text{const} - (n/4) \times \log f\text{O}_2 \quad (3)$$

To evaluate the importance of the C and the pressure effect on element partitioning we compare our data with $D(\text{metal/silicate})$ of Ni and Co at normal pressure [12]. For 7 and 10 kbar and 1350–1400°C in the presence graphite and (CO,CO₂) fluid and the given $f\text{O}_2$ metal partitions less strongly into the silicate melts than at atmospheric pressure in the absence of C (Table 1). At constant $f\text{O}_2$ the effect of pressure on the equilibrium (1) is given by

$$V(\text{MeO}_{n/2}, \text{liquid silicate}) - V(\text{Me}, \text{liquid metal}) > 0$$

The positive value of ΔV will cause the reaction (1) to shift to the left with increasing pressure, which effect we observe. However, the apparent partition coefficient will also be lowered if the activity of Me is lowered in the metal phase. The metal phase in our runs is 90–98 wt% of either Ni or Co, which translates into a mole fraction range of 0.90 to 0.96. Unless Ni or Co exhibit a strong negative deviation from ideality in metallic liquid the dilution effect will be much smaller than the effect observed. Another way to interpret this is by considering the effect of C species formation in melt or vapor phases on Ni and Co solubility in melt. In contrast to the behavior of Ir in the presence of graphite and (CO,CO₂) fluid the value of D_{Ni} and D_{Co} , does not show a strong composition dependence. Experiments on the Ir (metal) + (CO, CO₂) fluid C(graphite) + basaltic melt at 1–3 kbar 1200°C showed that formation of Ir-C-bearing complexes in the fluid phase as well as in the melt leads to a considerable decrease of $D(\text{metal/silicate})$ [13]. This variable is approximately two orders lower than those for C-absent system. We conclude that partitioning of Ni and Co between metal and silicate phase at pressure up to 10–15 kbar is not sensitive to the C content and most of the effect is due to pressure. However, metal separation during large-scale melting of the C-bearing mantle at high C activity the amount of C dissolved in the metal phase may be similar to that in our experiments (Table 1). It could affect the C depletion of the outer mantle, when molten C-bearing alloy and molten silicate underwent gravitational separation. Our experimental results support the hypothesis that C may be one of the light elements in the

OXYGEN FUGACITY AND PRESSURE ON Ni AND Co: A. A., Kadik and J. R. Holloway

molten outer core. Another factor to consider is the effect of C on Ni, Co, and Ir partitioning.

As it was found, unlike Ni and Co, Ir is the C-loving element. It could affect the mantle's ratio of Ni and Co to Ir. By measuring partition coefficient between Fe alloy and silicate melt (Allende CI chondrite as a starting material) Li and Agee [14] show that Ni and Co become less siderophile with pressure. Our experimental results on solubilities of Ni and Co in silicate melts in the presence of graphite and (CO,CO₂) fluid at 1350–1400°C and 7–15 kbar show that elements become more siderophile with increasing pressure. These data indicate that the pressure and the composition are actually key ingredients in the resolution of the mantle siderophile element problem.

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TABLE 1. Electron microprobe analysis of experimental products in the Ni and Co partitioning experiments and calculated Ni, Co- metal/silicate partition coefficient at P = 7–15 kbar, T = 1350–1400°C in the presence of graphite and at P = 1 bar, T = 1350°C for the carbon-free Ab-An-Di system [12].

Metal	P, bar	t, °C	–log fO ₂	NiO, CoO in melt, wt%	Ni, Co in metal, wt%	C in metal, wt%	D (met/sil)
Ni	10000	1350	8.18	1.01 ± 0.09	90.1 ± 0.05 (L) 99.4 ± 0.05 (D)	0.69 ± 0.05 (L) 1.46 ± 0.05 (D)	95.8 ± 7.5
Ni	10000	1400	7.85	0.92 ± 0.08	93.7 ± 0.05 (L) 97.1 ± 0.05 (D)	1.43 ± 0.05 (L) 1.74 ± 0.05 (D)	109.5 ± 9.5
Ni	15000	1350	7.64	n.d.	95.9 ± 0.05 (L)	1.54 ± 0.05 (L)	n.d.
Ni	1	1350	8.18	3.41 ± 0.015	99.9 ± 0.01		29.3 ± 0.1
Co	7000	1350	8.59		95.2 ± 0.05 (L) 97.7 ± 0.05 (D)	n d. n d.	8.9 ± 0.2
Co	1	1350	8.59	18.1 ± 0.06	99.9 ± 0.01		5.4 ± 0.1
Co	10000	1350	8.59	12.7 ± 0.2	n.d	n.d	7.9 ± 0.2
Co	10000	1400	7.85	14.1 ± 0.9	92.7 ± 0.05 (L) 86.5 ± 0.05 (D)	0.00 6.25 ± 0.05	7.0 ± 0.6
Co	1	1350	8.18	28.1 ± 0.1	99.9 ± 0.01		3.6 ± 0.1